ENHANCED BIOREMEDIATION IN CLAY SOILS

Ms. Zahra M. Zahiraleslamzadeh (FMC Corporation, San Jose, CA)
Jeffrey C. Bensch (GeoTrans, Rancho Cordova, CA)

ABSTRACT: This case study evaluates the full-scale in-situ application of an electron donor to enhance biodegradation of chlorinated solvents in clay soils and groundwater beneath an active light industrial property in a congested urban setting. A pilot test was successful by varying degrees in three test areas as shown by the production of biodegradation daughter products and microbial end products. The results of the pilot test were used to design and implement the full-scale remediation with minimal disturbances to ongoing business operations. After nine months of remediation monitoring, the trichloroethylene (TCE) is degrading to vinyl chloride (VC) and ethylene.

Organic acids, oxidation-reduction potential, and hydrogen monitoring results indicate that the microbial environment for reductive dechlorination was improved throughout the remediation area. TCE concentrations were significantly reduced, while cis-1,2 dichloroethylene concentrations increased then declined during the nine months following the full-scale application. Elevated sulfate concentrations also declined coincident with the reductions in TCE concentrations. VC and ethylene concentrations, however, have increased significantly. It is expected that VC will continue to degrade to ethylene, based on the observed increases in ethylene and other microbial end products. Additional applications of the electron donor are anticipated to complete the remedy. If necessary, a sequential in-situ aerobic remediation process may be required to fully degrade the VC.

INTRODUCTION

The biological reductive dehalogenation process of chlorinated solvents, such as tetrachloroethylene (PCE) and trichloroethylene (TCE), is an accepted viable groundwater remediation process. Various enhancements are available to stimulate biological activity and accelerate the dehalogenation process. Applying these enhancements to the subsurface for effective remediation can be difficult and uncertain. This paper presents the results of a full-scale remediation involving the injection of hydrogen release compound (HRC™) into a silty clay soil to stimulate biodechlorination of TCE in groundwater.

The Site is a 4.1-acre property with a 76,000 square-foot light-industrial retail building in a congested manufacturing neighborhood. The Site was used as agricultural land before the 1960s, then for various heavy manufacturing purposes through 1988. The building is currently leased to various light-industrial tenants.

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Topography at the Site is essentially flat with existing grades designed to control storm water runoff. The Site was unpaved until approximately 1980. Currently, most unoccupied areas are paved.

Site soils are a relatively homogenous silty clay from ground surface to a depth of approximately 45 to 50 feet. A gravelly sand unit, approximately 30 to 35 feet thick, underlies the silty clay. Saturated soils are first encountered approximately 17 feet below ground surface in the silty clay; while the depth to groundwater is approximately 7 to 10 feet below ground surface in wells screened in the silty clay. The groundwater flow velocity in the silty clay is approximately 10 feet per year.

The Site is impacted with volatile organic compounds (VOCs) in soil and shallow groundwater in the northeastern corner of the property (Figure 1).

FIGURE 1. Site Features

Anaerobic biodegradation of VOCs occurs in environments free of oxygen, where the parent chlorinated compound is progressively dechlorinated into daughter products. The process at this Site is the dechlorination of TCE into subsequent daughter compounds: cis-1,2 dichloroethylene (*cis*-1,2-DCE), vinyl chloride (VC), and ethylene. Microorganisms mediate this process using chlorinated compounds as electron acceptors and a source of hydrogen as the electron donor.

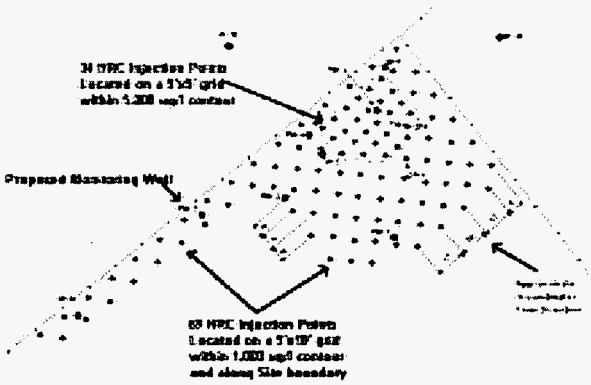
In the anaerobic biodechlorination process, the *cis*-1,2-DCE isomer is produced preferentially to the *trans*-1,2, DCE isomer (AFCEE 1996). As such, evidence for reductive dehalogenation of TCE can be obtained by observing the formation of *cis*-1,2-DCE in excess of *trans*-1,2 DCE, i.e., a *cis/trans* ratio greater than one. Increasing concentrations of VC and the microbial end product ethylene suggest the process is continuing toward completion.

TCE is among the most susceptible VOCs to reductive dechlorination because it is well oxidized (i.e., contains more chlorine atoms than hydrogen atoms). VC is the least susceptible to reductive dechlorination because it is the least oxidized of the daughter product compounds (Wiedemeier, et.al.,1996). Anaerobic destruction of VC has been observed in study cases (Cornuet, et.al., 2000), although it is more easily degraded in aerobic environments (Morse, et.al., 1998). The slower dechlorination of VC than TCE can result in an accumulation of VC.

Intrinsic biodegradation testing and evaluations were conducted at the Site in 1998 under Air Force Center for Environmental Excellence (AFCEE) similar protocols (Wiedemeier, et.al.,1996). Field parameters, organic and inorganic parameters, microbial end products, microbial community structure, and dechlorinated daughter products were evaluated. The dissolved oxygen, pH, and oxidation reduction potential (ORP) indicated that the Site was anaerobic, slightly reducing, and suggested that iron reduction may be the dominant redox process. The total organic carbon (TOC) concentrations and phospholipid fatty acids (PLFA) analyses of the microbial community indicated the Site could support a microbial population suitable to support anaerobic reductive dechlorination. The nitrate and sulfate concentrations were elevated with respect to optimal levels for reductive dechlorination. Sulfate concentrations ranging from 130 to 320 milligrams per liter (mg/L) indicated that sulfate reducing bacteria may compete for available hydrogen and hinder the reductive dechlorination processes. The dechlorination daughter products indicated the formation of the cis-1,2-DCE in groundwater at the Site. The ratio of the cis/trans-isomers indicated that this formation was likely due to a reductive dechlorination process. Microbial end-products were not present during the initial investigations. This indicated that any reductive dechlorination processes were not continuing to completion. In summary, the 1998 investigation indicated that biodegradation of VOCs occurred in the past, but it was very slow or in a dormant stage at the time of the evaluation.

Various remediation alternatives were evaluated, and HRC injection was selected because the HRC application is a simple procedure with minimal impacts to the existing property and current business activities.

A pilot study was implemented to evaluate the reductive dechlorination process in an isolated area at the Site (Zahiraleslamzadeh, 2000). HRC was applied in three adjacent areas with varying degrees of TCE impacts to groundwater. Following HRC application, significant reductions of TCE concentrations were observed with the accompanied increases in concentrations of daughter products and microbial end-products. The results of the pilot study indicated that reductive dechlorination could be stimulated at the Site and a full-scale HRC application was warranted.



MATERIALS AND METHODS

The scope of the full-scale remediation included injecting HRC through 103 direct-push points in the northeast corner of the property and along the northern property boundary to remediate an apparent TCE source area and to provide a barrier to downgradient TCE migration, respectively. As shown in Figure 2, the injection points were located on a 5-foot by 10-foot grid in most areas and a 5-foot by 5-foot grid in the apparent TCE source area.

The HRC application was conducted during 10 days of field work between May 16 and May 31, 2000. HRC injections were completed using a top-down approach starting approximately eight feet below ground surface and ending at 28 feet below ground surface. Top-down injection was accomplished using a steel rod perforated near the bottom four feet of pipe. After the perforated rod was driven to the desired depth, it was coupled to a high pressure hose and pump. A specific amount of HRC was injected and the rod was then driven to the next depth interval. Approximately 12 gallons of HRC were applied to each injection point.

FIGURE 2. HRC Injection Locations

Groundwater samples for baseline testing were collected from monitoring wells prior to HRC injection. Monitoring was conducted every other month for three months from July through November 2000, then at three month intervals in February 2001 and May 2001 (scheduled).

RESULTS AND DISCUSSION

The remediation efforts have been highly effective in reducing concentrations of TCE in groundwater. VC concentrations, however, have increased. Although this is expected as part of the biodechlorination process, increased VC concentrations are

a concern. Ethylene, the end-product of VC biodechlorination, has already increased in many wells, indicating that the bioremediation process is continuing to completion.

A natural attenuation screening analysis was performed in accordance with AFCEE protocol for each well and a summary is presented in Table 1. The results are useful in evaluating the suitability of a Site's geochemical condition for biodegradation of chlorinated compounds. The screening evaluation uses a scoring system based on a comparison of the monitoring results of natural attenuation parameters from a groundwater sample with an idealized result indicative of ongoing biodegradation.

Based on the results of the Natural Attenuation Screening Analysis, wells PW-1, PW-2, PW-3, PW-5, and W-2 show strong evidence of biodegradation, and wells W-8, W-9, W-35 and W-36 show limited evidence of biodegradation.

Time series trend evaluations for TCE, cis-1,2-DCE, VC, and ethylene provide an indication of the remediation effectiveness at each monitoring well. Time series graphs for monitoring wells PW-1 and W-9 are presented in Figure 3 and 4, respectively, to illustrate the remediation performance in areas of high and low biodechlorination activity.

High Biodechlorination Activity Illustrated by Well PW-1. Well PW-1 illustrates the strong evidence of increased TCE biodechlorination observed at many wells following the full-scale HRC implementation. The TCE and daughter product

Table 1. Screening Evaluation

Monitoring Wells	Total Screening Evaluation Score			
	May (1)	July (2)	Sept (3)	Nov (4)
PW-1	9	19	25	22
PW-2	13	18	23	22
PW-3	13	16	17	21
PW-5	17	22	23	21
W-2	11	16	25	25
W-8	8	15	14	13
W-9	10	11	14	13
W-35	11	NS	NS	12
W-36	15	NS	NS	14

	Score	Evaluation
(1) Baseline, prior to HRC injection		
(2) Approximately 2 months after HRC injection	0 to 5	Inadequate evidence of
(3) Approximately 4 months after HRC injection	6 to 14	Limited evidence of biodegradation
(4) Approximately 6 months after HRC injection	15 to 20	Adequate evidence of biodegradation
NS = Not Sampled	>20	Strong evidence of biodegradation

concentrations in well PW-1 changed dramatically by July 2000, when the level of TCE dropped an order of magnitude. A corresponding rise in the concentration of daughter products *cis*-1,2-DCE and VC further indicated enhanced TCE breakdown. By September 2000, the concentration of daughter product *cis*-1,2 DCE also began to

go down. The increase of ethylene concentrations indicated that the TCE dechlorination process was continuing to completion.

Figure 3. Time Series Evaluation Well PW-1

The anaerobic biodegradation indicators, organic acid concentrations, and field measurements support the conclusion of ongoing bioremediation at well PW-1 and the other wells with high scores in the screening evaluation. Organic acid concentrations rose in most of these wells after the HRC injection, and remained elevated throughout the November 2000 sampling event. This indicated the successful breakdown of HRC, and corresponding availability of organic acids and hydrogen for use by microbial populations.

Sulfate concentrations dropped to less than 10 mg/L in some wells coincident with high hydrogen concentrations and the significant declines in TCE concentrations. This observation is consistent with Yang and McCarty (1998), where competing methanogenic and dehalogenation reactions were studied with respect to hydrogen concentrations. Although the competing reactions may be an inefficient

use of the available hydrogen, the sulfate reduction has eliminated a competing biological reduction process. As such, the remaining hydrogen should now be more available for reductive dechlorination rather than sulfate reduction.

Field measurements gave further evidence of enhanced biodegradation occurring at these wells. Dissolved oxygen readings were low, indicating an anaerobic environment suitable for TCE degradation, while the pH measurements were typically lower than the optimal range of 5 to 9. ORP measurements remained in the optimal TCE-breakdown range during the July and September 2000 sampling events. By November 2000, the ORP had risen out of the optimal range for reductive dechlorination. The increasing ORP measurements may be indicative of a tapering-off of the reducing environment at the Site, which may be an early sign of the need for an additional HRC application in the future.

The hydrogen concentrations in some of the wells were extremely high during the six months following HRC injection. These elevated concentrations together with the initially low ORP measurements, indicate that methanogenic conditions existed through November 2000 in many of the wells. This is further supported by increasing methane concentrations in many of the wells. Hydrogen concentrations have began to decline, and the corresponding dechlorination performance versus methane production is being monitored.

Low Biodechlorination Activity Illustrated by Well W-9. Results from well W-9 show concentration trends with little indication of enhanced biodegradation. Well W-9 shows little variation in TCE, cis-1,2-DCE, trans-1,2-DCE, and VC concentrations throughout the months from May 1999 to November 2000. Well W-9 does exhibit a slight decrease in TCE concentration with slightly elevated concentrations of TCE breakdown products cis-1,2-DCE, VC, and ethylene in November 2000. This may be indicating enhanced biodegradation of TCE at well W-9, while the elevated TCE concentrations are maintained through desorption of TCE from the soil matrix.

Hydrogen concentrations at well W-9, and other low biodechlorination activity wells, were elevated above 2 nano-molar (nM); however, the organic acid concentrations remained below detection limits. This is an indication that the hydrogen concentrations may be due to factors other than a breakdown of HRC, because the HRC breakdown is typically accompanied by an increase in concentrations of organic acids. Methane, ethane, and ethylene concentrations remained low and unchanged, further indicating a lack of increased microbial activity at these wells. Sulfate concentrations remained high, further supporting the conclusion that enhanced biodegradation was not occurring at these wells.

Figure 4. Time Series Evaluation Well W-9

Field measurements at these wells indicated an environment capable of supporting enhanced biodegradation. DO measurements were close to 0.5 mg/L, and ORP measurements were below 100 mV. The ORP at well W-9 dropped from 145 to -28 mV from the baseline to the two-month monitoring event, then climbed back above 100 by November 2000. The pH measurements for most of these wells were generally around six, although the pH dropped at well W-9 in November 2000. Although the field measurements for these wells generally indicate an anaerobic environment suitable for TCE biodegradation, supporting evidence of enhanced biodechlorination at these wells was not found.

Given historical groundwater flow rates less than 10 feet per year, wells W-35 and W-36 lie well outside of the expected area of influence from the full-scale HRC implementation. It was expected, therefore, that wells W-35 and W-36 would not show near-term evidence of enhanced bioremediation from the addition of HRC. Well W-9, however, lies just to the north of the high-volume, 5-foot by 5-foot grid of

HRC injection points (Figure 2), and enhanced TCE-breakdown was expected. It is possible that the groundwater flow direction from May through November 2000 (towards the northwest) may have routed the effects of the HRC south of the well. More likely, however, the elevated TCE concentration at well W-9 is maintained through desorption of TCE from the soil matrix and future monitoring will indicate the effects of enhanced biodechlorination.

CONCLUSIONS

The HRC application enhanced the biological reductive dechlorination of TCE at the Site. The enhanced biodechlorination effectiveness is shown to be a function of the amount and proximity of HRC addition to a monitoring well. A high volume of HRC injected close to a well resulted in greater evidence of the dechlorination of TCE to completion. Wells PW-1, PW-3, and W-2 are located in the highest density of HRC injection locations and these wells exhibit the greatest evidence of biodechlorination. The limited biodechlorination at wells W-9, W-35, W-36, and W-8 appears to be due to the limited volume of HRC injected in the immediate vicinity of these wells.

The accumulation of VC in the Site groundwater is a recognized concern. It is expected that VC will accumulate through the dechlorination of cis-1,2 DCE, which is faster than the dechlorination of VC to ethylene. The elevated concentrations of VC are anticipated to decrease with time through continued dechlorination. The VC concentrations at many wells appear to have peaked and leveled off, while the ethylene concentrations are increasing at many wells. It is anticipated that the continued effects of the HRC will further stimulate the dechlorination of VC. If VC does not biodechlorinate to ethylene as anticipated, an aerobic environment may be needed to complete the destruction of this daughter product. Further monitoring efforts are ongoing to determine the long term effectiveness of the HRC application.

REFERENCES

Cornuet, Thomas S., C. Sandefur, W. Eliason, S. Johnson, C. Serna, 2000. *Accelerated Bioremediation of Chlorinated Compounds in Groundwater - Aerobic and Anaerobic Bioremediation of cis-1,2-Dichloroethene and VC*, International Conference on Remediation of Chlorinated and Recalcitrant Compounds, 2nd:2000, C2-4, Battelle Press, 2000.

Morse, Jeff J., Alleman, B.C., Gossett, J.M., Zindler, S.H., Fennell, D.E., Sewell, G., Vogel, C.M., 1998. *Draft Technical Protocol - A Treatability Test for Evaluating the Potential Applicability of the Reductive Anaerobic Biological In Situ Treatment Technology (RABITT) to Remediate Chloroethenes*, Department of Defense Environmental Security Technology Certification Program, 1998.

Wiedemeier, Todd H., M. Swanson, and D. Moutoux, E. K. Gordon; Drs. J. Wilson, B. Wilson, and D. Kampbell; J. Hansen and P. Haas; Dr. F. Chapelle, 1996. *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater.* Air Force Center for Environmental Excellence, November 1996.

Yang, Yanru, and P. McCarty, 1998. *Competition for Hydrogen within a Chlorinated Solvent Dehalogenating Anaerobic Mixed Culture*, Environmental Science & Technology, 1998.

Zahiraleslamzadeh, Zahra M., J. Bensch, 2000. *Enhanced Bioremediation Using Hydrogen Release Compound (HRC™) in Clay Soils*, International Conference on Remediation of Chlorinated and Recalcitrant Compounds, 2nd:2000, C2-4, Battelle Press, 2000.